GROUP-THEORETICAL APPROACH TO THE INVESTIGATION OF REACTION GRAPHS FOR HIGHLY DEGENERATE REARRANGEMENTS OF CHEMICAL COMPOUNDS

I. CRITERION OF THE CONNECTIVITY OF A GRAPH

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Abstract

We give a necessary and sufficient condition for a reaction graph of a degenerate rearrangement to be connected. This condition is formulated in terms of vertex stabilizers of the automorphism group of a molecular graph. The condition is illustrated on several examples, including the reaction graph of bullvalene. We consider different mathematical models for the construction of reaction graphs and state the problem: which of the models is more adequate?

1. Introduction

The investigation of reaction graphs for degenerate rearrangements of chemical compounds has gone through several stages. In the initial stage, concrete phenomena were investigated by chemists (see, for example, [1–3]) without the use of extensive mathematical tools. In the second stage, the group-theoretical technique was applied and, first of all, the excellent series of papers by Randić and his coworkers must be mentioned [4,5]. Their first results were obtained by *ad hoc* methods, but in the latest papers (see, for example, [6]), the authors were faced with the need to use powerful computer programs.

There are several other publications, for example [7–10], which can be characterised by the systematic use of the more complicated group-theoretical techniques (double cosets, suborbital graphs, and so on). In particular, Jones and Lloyd [10] have given a striking survey of different investigations of reaction graphs, which

is written in terms of permutation group theory. They have shown that for the most part, concrete results on reaction graphs can be obtained in a unified way by means of permutation group theory. This way is related to the often differently named notion: 2-orbits of permutation groups (in the sense of [11]), suborbital graphs (in the sense of [12,13]), and colour graphs, see [14].

Jones and Lloyd [10] have raised the following important question: how to determine when the reaction graph is connected? They have given a partial answer, but have also emphasized that an exhaustive answer is still unknown.

The goal of this paper is to give a complete answer to this question. In other words, we shall give a necessary and sufficient condition for a reaction graph to be connected. In turn, this condition is based on the known criterion from algebraic combinatorics for the connectivity of 2-orbital graphs. We apply this criterion to several interesting chemical reaction graphs, thereby giving an illustration of the technique developed. Particularly, we consider three different models of a reaction graph for the Cope rearrangement of bullvalene. Two of these models yield graphs with only 604,800 vertices, but not 1,209,600 vertices, as was stated in all previous publications and which can be obtained using the third model. We compare these different mathematical models for the construction of reaction graphs, and state the problem: which of the models is more adequate?

In this paper, we will use some elementary notions and facts from permutation group theory; references can be found in books [15–17] and papers [11–14,18–20].

We have tried to make this paper relatively self-contained, providing in sections 2 and 4 a small group-theoretical guidance. Section 3 contains the formulation of the main problem, while section 5 contains a criterion for the connectivity of a reaction graph (having the transitive automorphism group). Finally, the concrete example of the bullvalene case is considered in section 6. Section 7 includes a brief discussion of the presented results. Some additional comments related to the referee's opinion (Professor D.J. Klein) are collected in section 8.

2.   Preliminaries

We consider two kinds of chemical graphs: molecular and reaction graphs. A *molecular graph* represents a structural formula of an organic compound; it can have multiple edges and marked vertices (marks are the atom names). A *reaction graph* has different structural formulae as the vertices; two vertices are adjacent if there exists a rearrangement of a given type between them. If all vertices of a reaction graph represent the isomorphic structural formula, then we have a reaction graph of a *degenerate rearrangement*. If valencies of vertices of a reaction graph are greater than 1, then we have the case of a *highly* degenerate rearrangement. Finally, only those reaction graphs for which every edge represents a rearrangement of the same type will be considered.

Graphs will also be considered from a purely mathematical point of view. We shall usually speak of undirected graphs without loops and multiple edges (strict or simple graphs). In general, *graph* Γ is a pair $\Gamma = (V, E)$, where V is a set of vertices and E is a subset of the set $V^2 = \{(a, b) \mid a, b \in V\}$. In this case, we speak of a graph with *numbered* vertices (see section 4 for details).

Let $S(V)$ be a *symmetric* group of a set V; it consists of all permutations of the set V. If $|V| = n$ ($|V|$ is the cardinality of a set V), then the notation S_n is also used for the symmetric group $S(V)$. The notation $a^g = b$ means that a permutation g transforms an element a into b. For every subset $E \subseteq V^2$, we can consider the *induced action* of a permutation $g \in S(V)$: $E^g = \{(a^g, b^g) \mid (a, b) \in E\}$. For every graph $\Gamma = (V, E)$, an orbit of this induced action of $S(V)$ can be interpreted as an *"abstract" graph*. If $E^g = E$, then g is an *automorphism* of graph Γ. All automorphisms of Γ form an *automorphism group* $Aut(\Gamma)$ of Γ. Every automorphism group is a partial case of a *permutation group*, where permutation group G is any subgroup of the symmetric group $S(V)$. Usually, a permutation group is considered as a pair (G, V); in this situation, one can say that G *acts* on a set V and G has a *degree* $n = |V|$.

In addition to the symmetric group, we shall need the *alternating group* A_n, which consists of all even permutations of S_n, and the *dihedral group* D_n of degree n and order $2n$ (see below).

Let A be a subset of a group G and let every element of G be represented by a product of several elements of A (the sequence of these elements can contain the same element several times); then the group G is *generated* by A, and this fact can be noted as $G = \langle A \rangle$. For example, the dihedral group D_n can be obtained in the following manner: $D_n = \langle g, t \rangle$, where

$$g = (1, 2, \ldots, n) = \begin{pmatrix} 1 & 2 & 3 & \ldots & n \\ 2 & 3 & 4 & \ldots & 1 \end{pmatrix}$$

and

$$t = \begin{cases} (1,2)(3,n)(4,n-1) & \ldots & (k+1,k+3)(k+2), & \text{if } n = 2k+1, \\ (1,2)(3,n)(4,n-1) & \ldots & (k+1,k+2), & \text{if } n = 2k. \end{cases}$$

A subset $O \subseteq V$ is an *orbit* of permutation group (G, V) (a 1-orbit in the terminology of [11]) if for any two elements $a, b \in O$ there exists a permutation $g \in G$ such that $a^g = b$. The permutation group (G, V) is called *transitive* if V is its orbit, otherwise (G, V) is an *intransitive* group. Let $G_a = \{g \in G \mid a^g = a\}$ be a subset of those permutations of G which fix an element $a \in V$. G_a is a subgroup of G which is called a *stabilizer* of the element a in the group G. It is well known that for a transitive group (G, V), the *index* $[G : G_a] = |G| / |G_a|$ of a stabilizer of any element $a \in V$ coincides with the degree $|V|$ of the group G. Moreover, in this case the action of the group G on the set V is isomorphic (as a permutation group) to

the action of G on the set $\{G_a x \mid x \in G\}$ of different *cosets* of the subgroup G_a in the group G. The transitive permutation group (G, V) is *primitive* if for every $a \in V$ the stabilizer G_a is a *maximal* subgroup of group G (this means that $G = \langle G_a, g \rangle$ for any $g \notin G_a$). Otherwise, the transitive group (G, V) is called *imprimitive*.

3.   Formulation of the problem

Let us consider two different kinds of permutation groups. The groups of the first kind are automorphism groups of molecular graphs (or certain subgroups of these groups).

Let Γ be a molecular graph, V the set of its vertices and $Aut(\Gamma)$ its automorphism group. Let L be an n-element subset of the set V (in particular, it may be that $L = V$). Let the action of $Aut(\Gamma)$ on the set V be well defined (this means that L is *invariant* under the action of $Aut(\Gamma)$, i.e. L is the union of suitable orbits of $Aut(\Gamma)$) and faithful (this means that only the identical permutation of $Aut(\Gamma)$ fixes all vertices of L). The additional requirements for the set L will be considered later. Let $N = \{1, \ldots, n\}$. Then, we can number elements of L in such a way that different vertices of L will correspond to different numbers of N. The elements of $V \setminus L$ have not taken part in the numbering. Let $m = \mid Aut(\Gamma) \mid$ and $v = n!/m = [S_n : Aut(\Gamma)]$. One can easily show that in this situation the abstract graph Γ has exactly v different *numberings* $\Gamma_1, \Gamma_2, \ldots, \Gamma_v$ of its vertices. Let $\Omega = \{\Gamma_1, \Gamma_2, \ldots, \Gamma_v\}$. Then we can consider another kind of permutation group, namely the *induced* action of S_n on the set Ω.

Now let us consider a degenerate rearrangement of Γ. Then we can form a new *undirected reaction graph* $R = (\Omega, E)$ for this rearrangement in the following manner: two vertices Γ_i and Γ_j are adjacent in R if there exists an elementary rearrangement of a fixed (given) type directly between Γ_i and Γ_j. By definition, this reaction graph is invariant under the action of the symmetric group S_n. However, usually this graph is not connected, so it can be represented as a union of its disjoint connectivity components. The most ordinary case is when every component consists of only two vertices (two numberings). This is the case of the usual degenerate rearrangement, where each component adequately represents the *type* of rearrangement.

A more complicated and rare case is when the size of the connectivity components is greater than 2. Just this very case is by us called the case of a *highly* degenerate rearrangement. There are two most intriguing questions related to this case:

(1)   How large is the number of vertices in any connectivity component $\tilde{R}$ of a reaction graph R?

(2)   What is the full automorphism group $Aut(\tilde{R})$ of a graph $\tilde{R}$?

We shall not consider the second question here (it will be the subject of our following publications). We only stress that the group $Aut(R)$ can be determined (using the operation of the wreath product) if $Aut(\tilde{R})$ is known.

Thus, the first question will be the further focus of our present exposition. This question admits a partial formulation: when is the graph R connected? It must be mentioned here that from a chemist's point of view, namely the graph $\tilde{R}$ is really interesting (see below). Hence, in some situations the notion of a reaction graph is identified just with the graph $\tilde{R}$.

First of all, two relatively simple examples will be considered in order to give an illustration of all notions.

Example 1: 1, 2-shifts in the carbonium ion

This arrangement was first considered by Balaban et al. [2]. Two isomorphic graphs Γ_1 and Γ_2 are depicted in fig. 1. 1, 2-shift transforms Γ_1 into Γ_2 and vice versa.
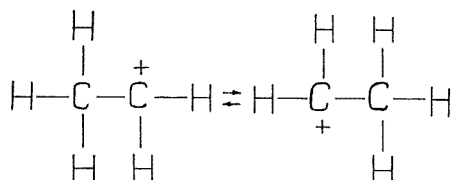

Fig. 1. 1, 2-shift in the carbonium ion.

Here, $Aut(\Gamma) \cong S_3 \times S_2$. The group $H = Aut(\Gamma)$ acts on the set V, which consists of five hydrogen and two carbon atoms. Let $L = V$. Then we have $v = 7!/12 = 420$; hence, $\Omega = \{\Gamma_1, \Gamma_2, \ldots, \Gamma_{420}\}$ is the set of all different numberings of Γ. Four of these numberings are symbolically depicted in fig. 2: Γ_1 and three other numberings
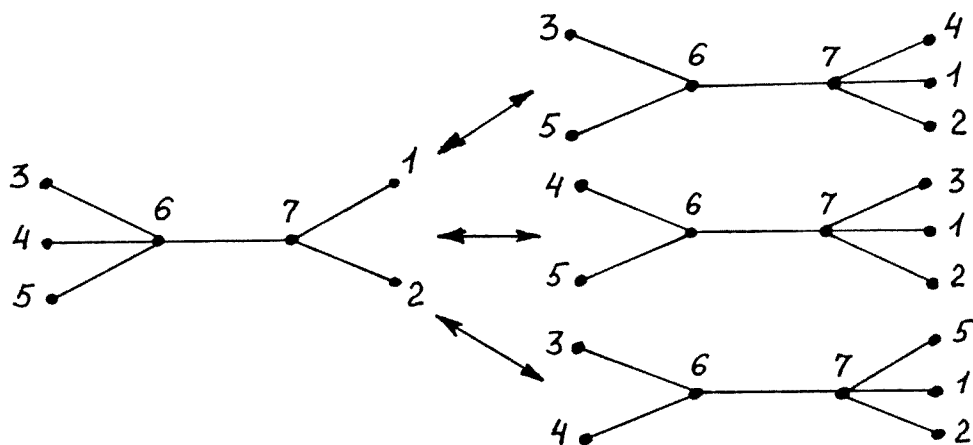

Fig. 2. Particular numbering of a carbonium ion (fig. 1) and three of its different 1, 2-shifts.

that can be directly obtained from Γ_1 via the 1, 2-shift. One can easily see that for these four numberings, the carbon atoms have a restricted set of numbers: $\{6, 7\}$. Evidently, this property will be fulfilled for all numberings of $\tilde{R}$. Hence, we can consider a subset Ω' of Ω; in this subset, all hydrogen atoms have numbers only from the set $\{1, 2, 3, 4, 5\}$. There are exactly $2 \cdot 5!/12 = 20$ numberings which satisfy this requirement. So, the connectivity component $\tilde{R}$ consists of at most 20 vertices. It was shown in [2] that $\tilde{R}$ actually consists of 20 vertices.

These vertices can be described in the following manner. Let us fix our attention on the carbon atom, having the number 6. Then, every numbering of Ω' is completely defined by a set of numbers of hydrogen atoms which are adjacent to the carbon atom having the number 6. Hence, every numbering of Ω' can be coded by means of 2- or 3-element subsets of the set $\{1, 2, 3, 4, 5\}$. There are exactly 20 such subsets; this implies that $|\Omega'| = 20$. Finally, using fig. 2, we can note that in $\tilde{R}$ a 3-element subset A can be adjacent only to a 2-element subset B, these subsets being adjacent if and only if $B \subset A$. We obtain that the graph $\tilde{R}$ is a bipartite cubic graph having 20 vertices. This graph is well known in algebraic combinatorics as the *doubled Petersen graph* or the *Desargues graph* [21] (see also [2,22]). One of the graphical presentations of $\tilde{R}$ is shown in fig. 3. We shall return to the consideration of this example in section 5.
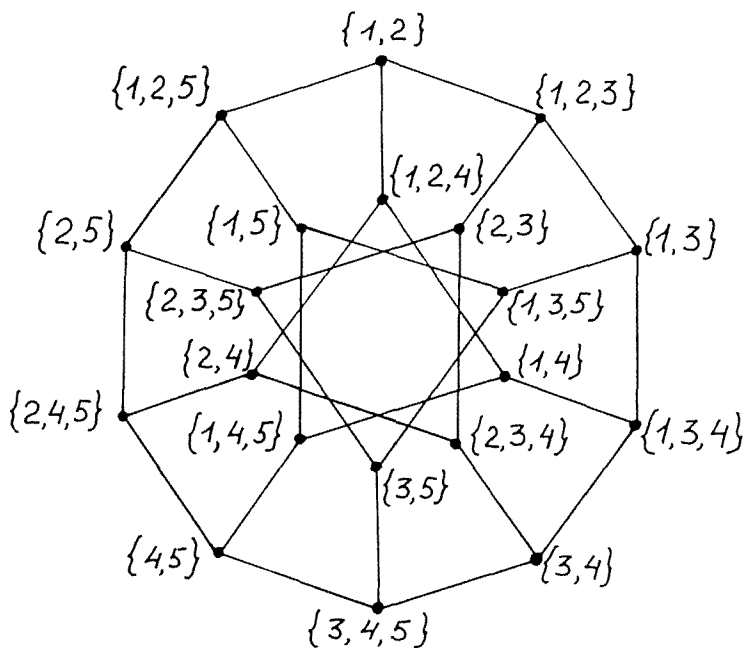

Fig. 3. The reaction graph for 1, 2-shifts in the carbonium ion is isomorphic to the doubled Petersen graph.

Example 2: 1,5-shifts in 1,2,3,4,5-pentachlorocyclopenta-2,4-diene

Here, molecular graphs Γ_1 and Γ_2, representing one edge of the reaction graph R, are depicted in fig. 4.
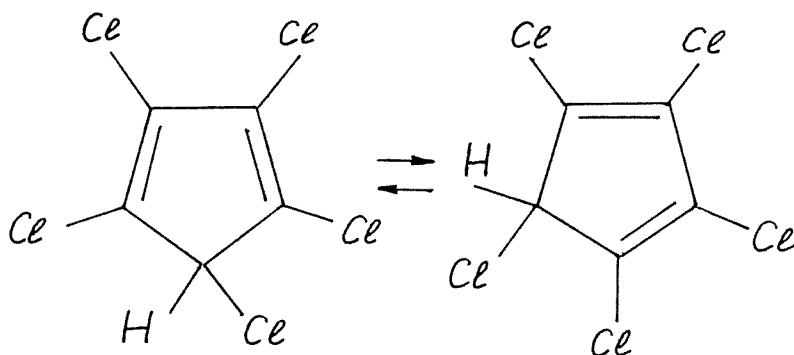

Fig. 4. 1,5-shifts in 1, 2, 3, 4, 5-pentachlorocyclopenta-2, 4-diene.

$Aut(\Gamma)$ is a permutation group of order 2. In the rearrangement, only carbon and hydrogen atoms are involved – hence, $n = 6$. This implies that $v = [S_6 : Aut(\Gamma)] = 6!/2 = 360$. The reaction graph consists of 360 vertices. It is easy to see that the connectivity component $\tilde{R}$ in this case includes only 5 vertices (see fig. 5). So, we once more
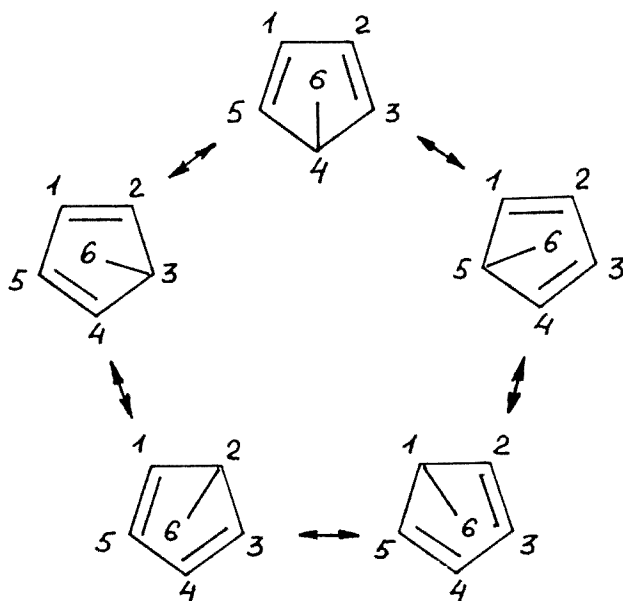

Fig. 5. Connectivity component of the reaction graph for 1, 2, 3, 4, 5-pentachlorocyclopenta-2, 4-diene.

have an example of a situation where $\tilde{R} \neq R$. In this situation, the connectivity component $\tilde{R}$ gives an adequate representation of the rearrangement process – it is really the desired reaction graph.

4.   2-Orbits of permutation groups

Let (G, Ω) be a permutation group and (a, b) a fixed pair of elements of Ω. A *2-orbit* Φ of a permutation group (G, Ω) is the set $\Phi = \{(a^g, b^g) \mid g \in G\}$. If (G, Ω) is a transitive group, then it always has a 2-orbit $\Phi_0 = \{(a, a) \mid a \in \Omega\}$, which is called a *trivial (reflexive)* 2-orbit. All other 2-orbits of a transitive group are called *nontrivial* or *antireflexive*.

With every 2-orbit Φ_i of a group (G, Ω) one can associate a graph $\Gamma_i = \Gamma(\Phi_i) = (\Omega, \Phi_i)$, having Ω as the set of vertices and Φ_i as the set of arcs. Graph Γ_0 includes only loops at every vertex. If the binary relation Φ_i is symmetric, then the graph Γ_i can be considered as undirected (in this case, we identify any pair (a, b) and (b, a) of opposite arcs with the edge $\{a, b\}$).

It is well known (see, e.g. [23]) that a transitive permutation group (G, Ω), having d antireflexive 2-orbits, is primitive if and only if all graphs Γ_i associated to antireflexive 2-orbits Φ_i, $1 \leq i \leq d$ of a permutation group (G, Ω), are connected.

Example 3

Let us consider the dihedral group D_6 of order 12. Below, a complete list of its permutations is presented:

$$g_1 = (1)(2)(3)(4)(5)(6), \qquad g_7 = (1)(2, 6)(3, 5)(4),$$
$$g_2 = (1, 2, 3, 4, 5, 6), \qquad g_8 = (1, 2)(3, 6)(4, 5),$$
$$g_3 = (1, 3, 5)(2, 4, 6), \qquad g_9 = (1, 3)(2)(4, 6)(5),$$
$$g_4 = (1, 4)(2, 5)(3, 6), \qquad g_{10} = (1, 4)(2, 3)(5, 6),$$
$$g_5 = (1, 5, 3)(2, 6, 4), \qquad g_{11} = (1, 5)(2, 4)(3)(6),$$
$$g_6 = (1, 6, 5, 4, 2, 2), \qquad g_{12} = (1, 6)(2, 5)(3, 4).$$

Using this list, one can easily construct a complete list of 2-orbits of the group D_6 in its natural action on the set $N = \{1, 2, 3, 4, 5, 6\}$, see fig. 6. In this action, D_6 has three antireflexive 2-orbits: Φ_1, Φ_2 and Φ_3. Two of these 2-orbits (Φ_2, Φ_3) give a disconnected graph; hence, the group D_6 is imprimitive. The graph Γ_1 is connected.

The natural question can be raised: when does a given 2-orbit lead to a connected graph? The answer to this question is well known in algebraic combinatorics.

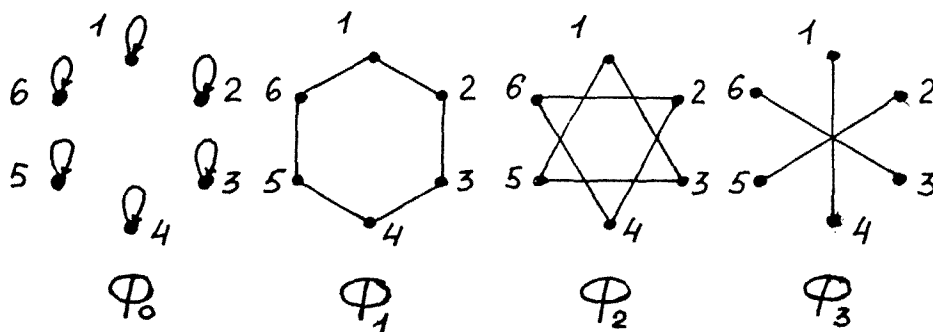As was noted in [16], the first publication of this result is due to Glauberman [24].

Fig. 6. Graphs associated to 2-orbits of the dihedral group D_6.

PROPOSITION 1

Let (G, Ω) be a transitive group, $a \in \Omega$, Φ_i any antireflexive 2-orbit of (G, Ω) for which $(a, b) \in \Phi_i$. Let $a^g = b$ for some $g \in G$. Then the graph $\Gamma_i = (\Omega, \Phi_i)$ is connected if and only if $\langle G_a, g \rangle = G$.

We shall also use the following more general result, which can be proved similarly to proposition 1.

PROPOSITION 2

Under the same conditions as in proposition 1, the number of vertices in a connectivity component of the graph $\Gamma_i = (\Omega, \Phi_i)$ is equal to the index $[\langle G_a, g \rangle : G_a]$.

We give an illustration of these propositions for the case of D_6. Here, $G = D_6$, $\Omega = N = \{1, 2, 3, 4, 5, 6\}$. Let $a = 1$, then $G_a = \{g_1, g_7\} = \langle g_7 \rangle = \langle (1) (2, 6) (3, 5) (4) \rangle$.

For 2-orbit Φ_1: $b = 2$, $g = g_8$, $\langle G_a, g \rangle = \langle g_7, g_8 \rangle = D_6$; hence graph Γ_1 is connected.

For 2-orbit Φ_2: $b = 3$, $g = g_9$, $\langle G_a, g \rangle = \langle g_7, g_9 \rangle \cong S_3$, where S_3 acts intransitively, having two 1-orbits: $\{1, 3, 5\}$ and $\{2, 4, 6\}$. $S_3 \neq G$; hence, graph Γ_2 is not connected, its connectivity component consists of $[\langle G_a, g \rangle : G_a] = 6/2 = 3$ vertices.

For 2-orbit Φ_3: $b = 4$, $g = g_{10}$, $\langle G_a, g \rangle = \langle g_7, g_{10} \rangle \cong K$, where K is a Klein four-group. $K \neq G$; hence, graph Γ_3 is not connected, its connectivity component consists of $[\langle G_a, g \rangle : G_a] = 4/2 = 2$ vertices.

Further, we shall consider the case where $G = S_n$ and Ω is the set of different numberings of a certain molecular graph Γ. In all known cases of highly degenerate rearrangements, a group $Aut(\Gamma)$ acts transitively on the set of numberings which can be *directly* obtained (by means of a rearrangement of *given* type) from the initial numbering Γ_1 of Γ. This implies that a reaction graph R is a suitable 2-orbit of the action (S_n, Ω).

5.   Criterion for connectivity of a reaction graph

Now we can formulate the main result of this paper (preliminary announcement, see [25]).

THEOREM 3

(Criterion for the connectivity of an edge transitive reaction graph).

Let Γ be a molecular graph for which a highly degenerate rearrangement of given type exists. Suppose exactly n vertices of Γ change their neighbourhood in Γ during the whole rearrangement process. Let $H = Aut(\Gamma)$ be an automorphism group of Γ, acting on the set $\{1, 2, \ldots, n\}$ and represented as $Aut(\Gamma_i)$ for a certain numbering Γ_i. Let Γ_i and Γ_j be two numberings of Γ which are adjacent in reaction graph R. Let $g : \Gamma_i \to \Gamma_j$ be an isomorphism between graphs Γ_i and Γ_j. Then:

(1)   the number of vertices in the reaction graph R is equal to the index $[S_n : H]$;

(2) R is connected if and only if $S_n = \langle H, g \rangle$;

(3)   the number of vertices in the connectivity component $\tilde{R}$ of the graph R is equal to the index $[\langle H, g \rangle : H]$.

The proof of the theorem can be easily obtained from propositions 1, 2 and the above-mentioned facts about 2-orbits of permutation groups and reaction graphs.

In order to give a preliminary illustration of theorem 3, we return to example 1. Two numberings Γ_2 and Γ_1 of the carbonium ion, representing the adjacent vertices of the reaction graph, are depicted in fig. 7.
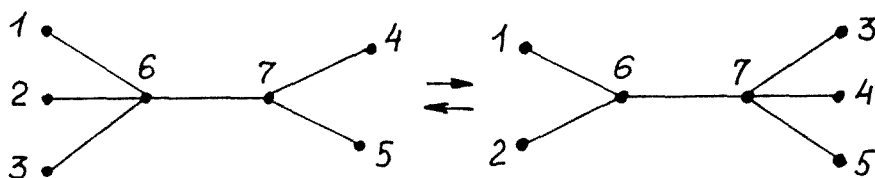

Fig. 7. Two numberings of the carbonium ion, which are adjacent in the reaction graph.

Here, $n = 7$, $H = Aut(\Gamma_2) \cong S_3 \times S_2 = \langle (1, 2, 3) (4, 5) (6) (7), (1, 2) (3) (4) (5) (6) (7),$ $(1) (2) (3) (4, 5) (6) (7) \rangle$. There are twelve different isomorphisms from numbered graph Γ_2 to numbered graph Γ_1. One of them can be immediately observed from fig. 7:

$$g = \begin{pmatrix} 1\ 2\ 3\ 4\ 5\ 6\ 7 \\ 3\ 4\ 5\ 1\ 2\ 7\ 6 \end{pmatrix} = (1, 3, 5, 2, 4)(6, 7).$$

The group $\langle H, g \rangle$ is obviously intransitive, having two orbits: $\{1, 2, 3, 4, 5\}$ and $\{6, 7\}$. Let us consider the action of $\langle H, g \rangle$ on the set $\{1, 2, 3, 4, 5\}$. It is a transitive group of prime degree $n = 5$, hence it is primitive; this group contains a transposition. It is well known that a primitive permutation group which contains a transposition is a symmetric group. Hence, the action of $\langle H, g \rangle$ on $\{1, 2, 3, 4, 5\}$ coincides with S_5, and $\langle H, g \rangle = S_5 \times S_2$. Using theorem 3, we obtain that the connectivity component of the reaction graph contains 20 vertices. We have obtained the same result as in section 3, where the reaction graph was considered on the "visual" level.

Example 2 provides an illustration of a similar situation. Here (see fig. 5), $n = 6$, $H = Aut(\Gamma_1) = \langle (1, 2)(3, 5)(4)(6) \rangle$,

$$g = \begin{pmatrix} 1 \ 2 \ 3 \ 4 \ 5 \ 6 \\ 2 \ 3 \ 4 \ 5 \ 1 \ 6 \end{pmatrix} = (1, 2, 3, 4, 5)(6). \quad \langle H, g \rangle = D_5 \neq S_5.$$

Hence, the reaction graph is not connected and its connectivity component consists of $[D_5 : H] = 10/2 = 5$ vertices. As in example 1, the result of using theorem 3 agrees with the result of the direct construction of the connectivity component.

It is clear that a systematic application of theorem 3 requires solving the following problem: to describe the permutation group generated by a given set of its permutations. This problem can be solved in a general case with the aid of a computer (see, for example, [26, 27]). However, for all considered cases it was always possible to find a group $\langle H, g \rangle$ using only hand computations. These computations are based on combining general facts from permutation group theory [15] with concrete information about primitive permutation groups of the given degree (see, e.g. [28]).

Usually, the group H, which is mentioned in theorem 3, is the full automorphism group $Aut(\Gamma)$ of the corresponding molecular graph Γ. In principle, it is possible to use in the role of H certain subgroups of $Aut(\Gamma)$, especially the subgroup of index 2, which is induced by the proper rotations of the spatial model of Γ (in this case, $Aut(\Gamma)$ is induced by rotation and reflections). This latter case reflects the fact that we distinguish between the spatial model of Γ and its mirror image. From a mathematical point of view, we can use as H any permutation group. However, one can take into account that changing H actually leads to a new mathematical model for the rearrangement process. We shall compare two different models as a concrete example in the next section.

Finally, we want to mention one more problem, related to the selection of the set $L = \{1, 2, \ldots, n\}$. In some cases, there are several possibilities to establish this set and, at first sight, the mode of the connectivity component $\tilde{R}$ depends on the set L. However, there is no real dependence of $\tilde{R}$ on L. For simplicity, we do not give a rigorous proof of the corresponding proposition here, restricting ourselves to one example.

Let us again consider example 2. Here, we can put $L = \{1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11\}$, where $7 - 11$ are the numbers of five chlorine atoms. Then, the reaction graph R has $[S_{11} : H] = 11!/2 = 19,958,400$ vertices, but the connectivity component $\tilde{R}$ consists of the same number $(= 5)$ of vertices.

6.   The case of bullvalene

The Cope rearrangement of bullvalene $C_{10}H_{10}$ is, of course, the most famous example of a highly degenerate rearrangement. The structure of bullvalene was designed by von E. Doering and Roth [29]; it was synthesized by Schröder [1] (one can find the very intriguing history of the name bullvalene in [30], p. 131). The reaction graph R of bullvalene is one of the largest in chemical graph theory: for this reason, it was called the Monster graph [6].

During many years, it was accepted that this graph consists of $10!/3 = 1,209,600$ vertices (see, e.g. [31]). Such a decision can follow from the opinion that only the symmetries of C_3 correspond to free molecular motions (rotations) without the breaking (or extreme distortion) of bonds. In this case, the skeleton and its mirror image are distinguishable. From our point of view, the full symmetry group of the spatial model of the graph Γ is isomorphic to its full automorphism group $Aut(\Gamma)$, i.e. to the symmetric group S_3. Unfortunately, in the literature we could not find arguments for the precise decision, but some arguments were kindly provided to us by Professor D.J. Klein [32]. His arguments are related, partially, to the Dreiding models and to the possible solution of the Schrödinger equation for bullvalene. For this reason, it is natural to consider simultaneously two different models of the rearrangement process (in the sense of section 5). Two numberings Γ_1 and Γ_2 of the molecular graph Γ of bullvalene are depicted in fig. 8 (hydrogen atoms are omitted); the Cope rearrangement transforms Γ_1 into Γ_2 and vice versa.
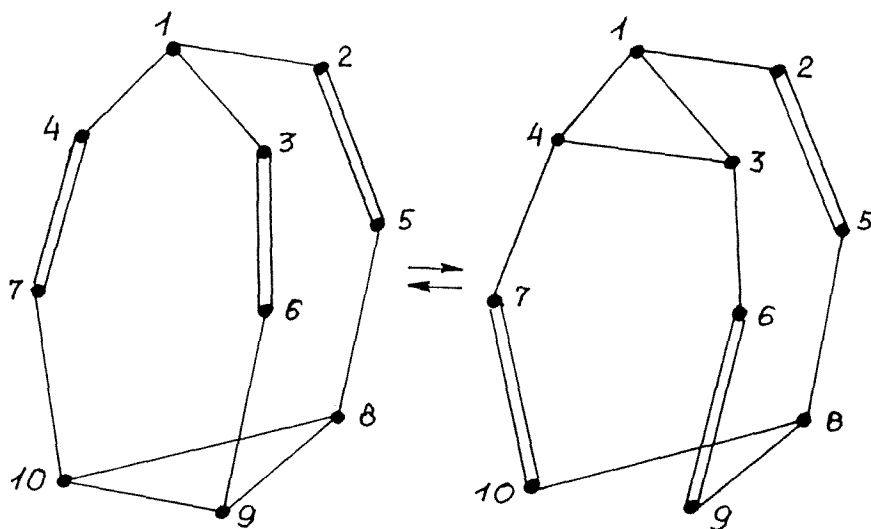

Fig. 8. Cope rearrangement in bullvalene.

Here, $n = 10$, $Aut(\Gamma_1) = \langle h_1 = (1)\,(2, 3, 4)\,(5, 6, 7)\,(8, 9, 10)$, $h_2 = (1)\,(2, 3)\,(4)\,(5, 6)$ $(7)\,(8, 9)\,(10)\rangle$. There are exactly six permutations which transform Γ_1 into Γ_2; one of these is

$$g = \begin{pmatrix} 1 & 2 & 3 & 4 & 5 & 6 & 7 & 8 & 9 & 10 \\ 8 & 5 & 9 & 10 & 2 & 6 & 7 & 1 & 3 & 4 \end{pmatrix} = (1, 8)\,(2, 5)\,(3, 9)\,(4, 10)\,(6)\,(7).$$

Now we shall consider the rearrangement process via two different models.

Model I. We put $H = Aut(\Gamma)$; hence, theorem 3 will be applied in a natural way. Let v be the number of vertices of a reaction graph R. Then, $v = [S_{10} : Aut(\Gamma_1)]$ $= [S_{10} : S_3] = 10!/6 = 604{,}800$.

Let us investigate the group $\langle H, g \rangle = \langle h_1, h_2, g \rangle$. The group $\langle h_1, g \rangle$ is clearly transitive; hence, $\langle H, g \rangle$ is also transitive. Then let us proceed with a few easy calculations.

$$t_1 = h_1^{-1} g = (1, 8, 4, 9)\,(2, 10, 3, 5, 7, 6),$$

$$t_2 = t_1 h_1^{-1} = (1, 10, 2, 9)\,(3, 7, 5, 6, 4, 8),$$

$$t_3 = t_1 t_2 = (1, 3, 6, 9, 10, 7, 4)\,(2)\,(5)\,(8).$$

Hence, $t_3 \in \langle H, g \rangle$ and t_3 is a permutation of prime order 7. This implies that $\langle H, g \rangle$ cannot be imprimitive (the order of an imprimitive group of degree 10 is obviously equal to $2^\alpha 3^\beta 5^\gamma$ for suitable α, β, γ); so $\langle H, g \rangle$ is a primitive permutation group. The order of $\langle H, g \rangle$ has a prime divisor 7. Using the list of primitive groups of degree 10 from [28], we conclude that $\langle H, g \rangle$ coincides with A_{10} or S_{10}. Taking into account that $h_2 \in \langle H, g \rangle$ and that h_2 is an odd permutation, we obtain $\langle H, g \rangle = S_{10}$. Hence, R is a connected graph, $\tilde{R} = R$ and $\tilde{R}$ contains 604,800 vertices.

Model II. Now we omit permutations from $Aut(\Gamma)$ corresponding to the improper rotations ($=$ reflections) of the 3D-spatial model of graph Γ_1, i.e. we put $H = (Aut(\Gamma_1))^{pos}$, where F^{pos} denotes the subgroup of a group F consisting only of even permutations. This means that now there are $v = [S_{10} : A_3] = 10!/3$ possible isomers, each of these isomers corresponding to some coset class of the group S_{10} over the subgroup $A_3 = H = (Aut(\Gamma_1))^{pos} = \langle h_1 \rangle$. These isomers cannot be interpreted on the purely graph-theoretical level, but if we can find a certain 3D-structure of the molecular graph Γ which is *chiral*, then all coset classes will be in one-to-one correspondence with different numberings of this 3D-structure. However, this geometrical point of view will not be considered here (it will be discussed elsewhere), and we shall remain on the formal group-theoretical level. Among the six permutations which transform Γ_1 into Γ_2, three permutations are even (e.g. the permutation g) and three permutations are odd (e.g. the permutation $\tilde{g} = h_1 h_2 g = (1, 8)\,(2, 5)\,(3, 10),\,(4, 9)\,(6, 7)$). This leads to the consideration of two new different cases.

Model IIA. Here, $H = \langle h_1 \rangle$, cosets H and Hg represent a pair of adjacent vertices of a reaction graph R. The calculations, made as above (model I), show that $\langle H, g \rangle = A_{10} \neq S_{10}$. Hence, in this situation R is not a connected graph and a connectivity component $\tilde{R}$ of R consists of $[A_{10} : A_3] = 10!/6 = 604,800$ vertices.

Model IIB. Here, $H = \langle h_1 \rangle$, cosets H and $H\tilde{g}$ represent a pair of adjacent vertices of a reaction graph R. We must investigate the group $\langle H, \tilde{g} \rangle = \langle h_1, \tilde{g} \rangle$. This group is transitive, too. We calculate $t_4 = h_1 \tilde{g} = (1, 8, 4, 5, 7, 2, 10)\,(3, 9)\,(6)$; t_4 has order 14. The same arguments as above show that $\langle H, \tilde{g} \rangle$ is a primitive permutation group. Then we show that $\langle H, \tilde{g} \rangle = A_{10}$ or S_{10}, and, according to the fact that $\tilde{g} \in \langle H, \tilde{g} \rangle$ is an odd permutation, we conclude that $\langle H, \tilde{g} \rangle = S_{10}$. Hence, in this case the reaction graph R is connected, $\tilde{R} = R$ and $\tilde{R}$ consists of $10!/3 = 1,209,600$ vertices.

Thus, we have three different models: the first and second models imply that the size of the connectivity component is equal to $10!/6$, while the third model implies a size $10!/3$. The natural question arises: which model is more adequate? We do not want to discuss this question in full here. As was mentioned, it must be the topic of a special paper. The only aim of this section was to demonstrate, on the classical case of bullvalene, the possibilities of the group-theoretical technique.

7. Conclusions

In this paper, we have given a criterion for the connectivity of a vertex- and edge-transitive graph and have shown how this criterion can be transformed into a criterion for the connectivity of a reaction graph of highly degenerate rearrangements. We have demonstrated the abilities of the criterion on several examples. It turns out that in the case where different vertices of a reaction graph correspond to different numberings of a molecular graph, there is no difficulty in describing the connectivity component of the reaction graph.

The case of bullvalene demonstrates another situation: there are three different models to construct the reaction graph here. Two of these models give $v = 10!/6$ vertices in a connectivity component, while the third gives a twice larger size of the component. The question about which is the most adequate model remains open here. We shall consider it in a special publication.

The case of a Cope-type rearrangement in the P_7^{3-} ion is very similar to the bullvalene case. Here, a subgroup $H = Aut(\Gamma)$ consists only of even permutations, while a permutation g, which transposes two different numberings (adjacent in a reaction graph), is odd. For this reason, it is easy to show that model I produces $\tilde{R} = R$ with $v = 7!/6 = 840$ vertices, while model II gives $\tilde{R} = R$ too, but in the latter situation, $v = 7!/3 = 1680$ vertices. Model II was investigated in [6] with the aid of a computer. The connectivity of a reaction graph was proved in [6] on a combinatorial basis. Additionally, it was shown that the reaction graph has a diameter $d = 14$ and that two vertices, which represent the enantiomers, corresponding to the same numbering

of the molecular graph, are antipodal, i.e. the distance between these two vertices takes the maximal value of 14.

Thus, one also faces the analogous problem of comparing the two possible models. The authors of [6] stressed that their model represents only the hypothetical mechanism of a rearrangement process, but they did not provide the direct arguments why especially this model was preferred. We think that the question merits discussion, as in the previous case of bullvalene. We want to stress that in all other cases of highly degenerate rearrangements that were considered in the literature, model I was always preferred. Perhaps this model is not necessarily adequate in all situations, but the preference must be motivated on a sufficiently rigorous level, using both chemical and mathematical arguments. Finally, we draw the reader's attention to the fact that the question of the size of a connectivity component of a reaction graph was also discussed in [6]. In particular, it was mentioned in ref. [17] of this paper that Dr. R.A. Davidson and Prof. P.S. Wharton had clarified that the bullvalene reaction graph is connected and consists of 10!/3 vertices; unfortunately, no arguments for such a decision were given. We agree with the authors of [6] that the most interesting case will be if the reaction graph constructed by means of model I (in the sense of this paper) contains two connectivity components. No example having this feature is known to us. However, such an example, if it really exists, will demonstrate a new kind of chirality: two separate fluxional worlds of "numerational isomers".

As was mentioned, this paper is the first in a planned series of publications. In the forthcoming papers, we hope to consider several interesting large reaction graphs. The question about the full automorphism group of reaction graphs will also be treated, and a new technique for finding the so-called 2-closure of permutation groups will be applied. This technique was developed in close collaboration with M.E. Muzichuk. Preliminary information about this technique is presented in [20].

8.   Additional comments

This short section has been added to the revised version of our paper in reply to the (non-anonymous) referee's review, written by Douglas J. Klein. A number of changes proposed in his review helped us to make the text clearer. In addition to this review, we received a copy of an unpublished paper [33], which was written a decade before the present paper. It follows from this manuscript and from the above-mentioned comment of Dr. R.A. Davidson that model IIB (in our notation) is the most preferable; this means that in Randić–Klein's opinion, the connectivity component of the reaction graph consists of 10!/3 vertices.

The only question is the selection of a permutation in model IIB which represents a coset adjacent to the coset H. Instead of our permutation $\tilde{g} = (1, 8)\,(2, 5)\,(3, 10)\,(4, 9)\,(6, 7)$, Randić and Klein use the other permutation $(1, 8, 4, 5, 7, 2, 10)\,(3, 9)\,(6)$ – it is $t_4 = h_1\,\tilde{g}$ in our notation. Obviously, every permutation of $H\tilde{g}$ can be used as a representative; hence, there is really no essential difference in our selections.

Another interesting detail lies in the fact that the authors of [33] have previously used just the permutation g and hence model IIA in our notation. This surprising coincidence of our ways seems to be pleasant for both groups.

In this connection, we want to stress once again that our consideration of the bullvalene case in section 6 is an illustrative one. We deliberately compare three different models in order to expose vividly all possible difficulties. The selection of an adequate model requires two separate decisions: one about the subgroup H and one about the coset which is adjacent to H in the reaction graph. These questions are of a special nature, which is not the subject of this paper. Some of them will be discussed in [34], but the complete analysis of the bullvalene case is worthy of careful consideration in a special paper. In our opinion, such a paper could be the result of a collaboration of both groups having experience in this field.

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References

[1]   G. Schröder, Chem. Ber. 97(1964)3140.
[2]   A.T. Balaban, D. Farcásiu and R. Bánicá, Rev. Roum. Chim. 11(1966)1205.
[3]   M. Gielen, in: *Chemical Applications of Graph Theory*, ed. A.T. Balaban (Academic Press, 1976), p. 261.
[4]   M. Randić, Croat. Chem. Acta 49(1977)643.
[5]   M. Randić, D.J. Klein, V. Katović, D.O. Oakland, W.A. Seitz and A.T. Balaban, Stud. Phys. Theor. Chem. 54(1987)266.
[6]   M. Randić, D.O. Oakland and D.J. Klein, J. Comput. Chem. 7(1986)35.
[7]   Th.D. Bouman and C. Trindle, Theor. Chim. Acta 37(1975)217.
[8]   I. Ugi, J. Dugundji, R. Kopp and D. Marquarding, *Perspectives in Theoretical Stereochemistry*, Lecture Notes in Chemistry, Vol. 36 (Springer, Berlin, 1984).
[9]   J. Brocas, M. Gielen and R. Willem, *The Permutational Approach to Dynamic Stereochemistry* (McGraw–Hill, New York, 1983).
[10] G.A. Jones and E.K. Lloyd, in: *Chemical Applications of Topology and Graph Theory*, ed. R.B. King, Studies in Physics and Theoretical Chemistry, Vol. 28 (Elsevier, 1983).
[11] L.A. Kalužnin and M.H. Klin, Math. USSR Sbornik (Engl. Transl.) 16(1972)95.
[12] P.J. Cameron, in: *Combinatorics*, ed. M. Hall and J.H. van Lint (Reidel, Dordrecht, 1975), p. 419.
[13] T. Tsuzuku, *Finite Groups and Finite Geometries*, Cambridge Tracts in Mathematics, Vol. 78 (Cambridge, 1982).
[14] P.M. Neumann, in: *Topics in Group Theory and Computation*, ed. M.P.J. Curran (Academic Press, London, 1977), p. 82.

[15] H. Wielandt, *Finite Permutation Groups* (Academic Press, New York–London, 1964).

[16] E. Bannai and T. Ito, *Algebraic Combinatorics I. Association Schemes* (Benjamin/Cummings, London, 1984).

[17] M.Ch. Klin, R. Pöschel and K. Rosenbaum, *Angewandte Algebra für Mathematiker und Informatiker. Einführung in gruppentheoretische-kombinatorische Methoden* (DVW, Berlin, 1988).

[18] M.H. Klin and I.A. Faradžev, in: *Investigations in Applied Graph Theory* (Nauka, Novosibirsk, 1986), p. 59 (in Russian).

[19] A.A. Ivanov, M.H. Klin and I.A. Faradžev, Graphs and Comb. 6(1990)303.

[20] M.H. Klin, M.E. Muzichuk and I.A. Faradžev, in: *Algebraic Theory of Combinatorial Objects*, ed. I.A. Faradžev, A.A. Ivanov and M.H. Klin (Kluwer, Dordrecht, 1991), to appear.

[21] A.E. Brouwer, A.M. Cohen and A. Neumaier, *Distance Regular Graphs* (Springer, Berlin, 1989).

[22] M. Randić, Int. J. Quant. Chem. 15(1979)663.

[23] C.C. Sims, Math. Z. 95(1967)76.

[24] G. Glauberman, Pac. J. Math. 29(1969)137.

[25] M.H. Klin, in: *Int. Conf. on Algebra. Applied and Computer Algebra*, Theses of Lectures (Novosibirsk, 1989), p. 31.

[26] P.M. Neumann, London Math. Soc. Lect. Notes Ser. 121(1986)59.

[27] C.A. Brown, L. Finkelstein and P.W. Purdom, SIAM J. Comput. 18(1989)1037.

[28] C.C. Sims, in: *Computational Problems in Abstract Algebra* (Pergamon, London, 1970), p. 169.

[29] W. von E. Doering and W.R. Roth, Tetrahedron 19(1963)715.

[30] A. Nickon and E.F. Silversmith, *Organic Chemistry. The Name Game* (Pergamon, London, 1987).

[31] J.F.M. Oth, K. Mullen, J.M. Gilles and G. Schröder, Helv. Chim. Acta 57(1974)1415.

[32] D.J. Klein, private communication.

[33] M. Randić and D.J. Klein, Graph-theoretical analysis of the bullvalene rearrangement, Manuscript (1981), unpublished.

[34] M.H. Klin and N.S. Zefirov, Group-theoretical approach to the investigation of reaction graphs for highly degenerate rearrangements of chemical compounds. II. Fundamental concepts, submitted.